

Hair Dye Composition

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to a hair dye composition having excellent dyeing power, being capable of imparting a wide range of colors to the hair without losing their vividness, and showing less color fade over time.

2. Background Art

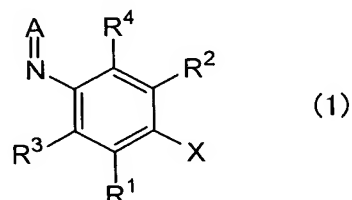
10 Hair dyes can be classified by a dye to be used therefor, or by whether they have bleaching action of melanin or not. Typical examples include a two-part permanent hair dye composed of a first part containing an alkali agent, an oxidation dye and optionally a direct dye
15 such as a nitro dye and a second part containing an oxidizing agent; and a one-part semi-permanent hair dye containing an organic acid or an alkali agent, and an acid dye, basic dye or direct dye such as a nitro dye.

20 The above-described permanent hair dye is however accompanied by the drawback that the color tone imparted by an oxidation dye is not so vivid. Use of a nitro dye or cationic dye for a two-component hair dye containing an oxidizing agent has been attempted in order to produce various color tones (refer to, for example, Japanese Patent
25 Laid-Open Nos. 271435/1994 and 2001-261535). A hair dye

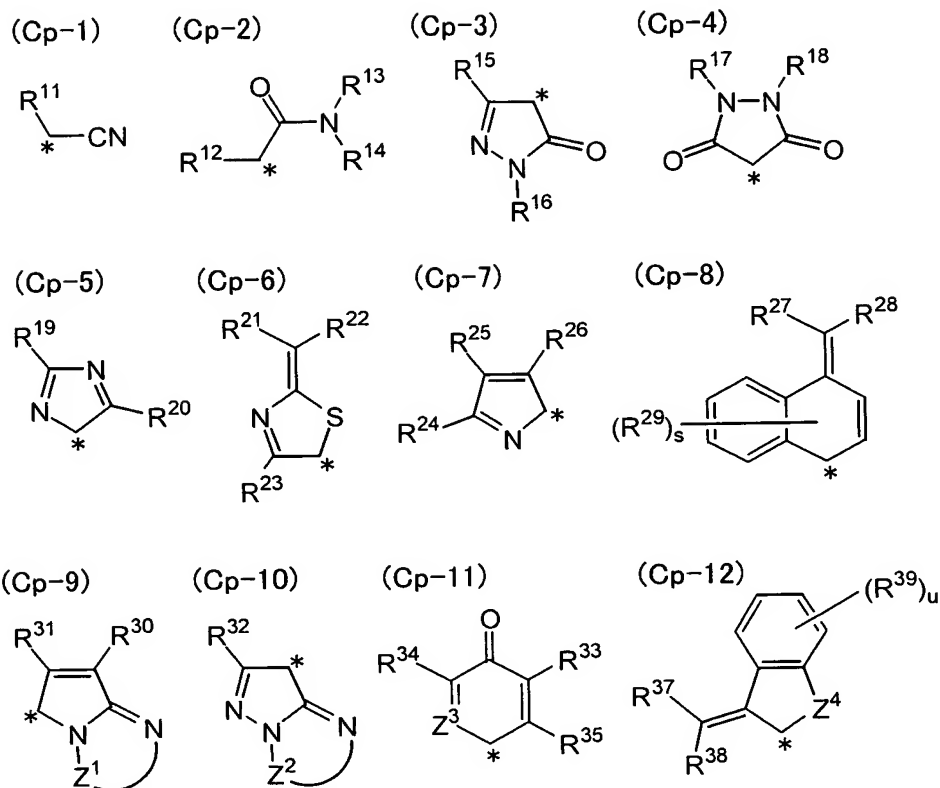
added with a nitro dye develops a vivid color just after dyeing, but color fades away remarkably over time and tends to be dull. Use of a cationic dye, on the other hand, involves such problems that it is easily decomposed when mixed with a peroxide serving as an oxidizing agent and it cannot readily be used in combination with an anionic polymer.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a hair dye composition comprising a dissociative direct dye represented by the following formula (1):



wherein, R^1 , R^2 , R^3 and R^4 each independently represents a hydrogen atom or a substituent, X represents a hydroxyl group or $-NHSO_2R^5$, in which R^5 represents an alkyl, aryl or heterocyclic group, and A represents a group represented by any one of the below-described formulas (Cp-1) through (Cp-12) with the proviso that the above-described groups may have one or more substituents:



(in formulas (Cp-1) through (Cp-12), * is a position bonding to the nitrogen atom in formula (1),

in formula (Cp-1), R^{11} represents a cyano group, acyl group, aryl group, heterocyclic group or a group $-C(R^{101})=C(R^{102})-R^{103}$, in which R^{101} , R^{102} and R^{103} each independently represents a hydrogen atom or a substituent with the proviso that at least one of R^{102} and R^{103} is an electron attractive group having a Hammett σ_p value of 0.1 or greater,

in formula (Cp-2), R^{12} represents a cyano, alkoxy carbonyl, carbamoyl, aryl or heterocyclic group, and R^{13} and R^{14} each independently represents a hydrogen atom or an alkyl, aryl or heterocyclic group,

in formula (Cp-3), R^{15} represents a hydrogen atom or an alkyl, aryl, heterocyclic, amino, alkylamino, arylamino, heterocyclic amino, alkoxy, acylamino, alkoxy-carbonylamino, ureido, alkoxy-carbonyl, carbamoyl or cyano group, and R^{16} represents a hydrogen atom or an alkyl, aryl or heterocyclic group,

in formula (Cp-4), R^{17} and R^{18} each independently represents a hydrogen atom or an alkyl, aryl or heterocyclic group,

in formula (Cp-5), R^{19} and R^{20} each independently represents a hydrogen atom or an alkyl, aryl or heterocyclic group,

in formula (Cp-6), R^{21} and R^{22} each independently represents a cyano, carbamoyl, alkoxy-carbonyl, alkylsulfonyl or arylsulfonyl group, and R^{23} represents a hydrogen atom or an alkyl, aryl or heterocyclic group,

in formula (Cp-7), R^{24} , R^{25} and R^{26} each independently represents a hydrogen atom or a substituent,

in formula (Cp-8), R^{27} and R^{28} each independently represents a cyano, carbamoyl, alkoxy-carbonyl, alkylsulfonyl or arylsulfonyl group, R^{29} represents a substituent, and s stands for an integer of from 0 to 6,

in formula (Cp-9), R^{30} and R^{31} each independently represents a hydrogen atom or a substituent, and Z^1

represents an atomic group necessary for the formation of a

6-membered ring together with $\text{N}=\text{C}=\text{N}$,

in formula (Cp-10), R^{32} represents a hydrogen atom or a substituent, and Z^2 represents an atomic group necessary for the formation of a 6-membered ring together with $\text{N}=\text{C}=\text{N}$,

5 in formula (Cp-11), R^{33} , R^{34} and R^{35} each independently represents a hydrogen atom or a substituent, Z^3 represents a nitrogen atom or $-\text{C}(\text{R}^{36})=$, and R^{36} represents a hydrogen atom or a substituent, with the proviso that when Z^3 represents $-\text{C}(\text{R}^{36})=$, R^{34} and R^{36} may be coupled to form a 5-
10 membered or 6-membered ring, and

in formula (Cp-12), R^{37} and R^{38} each independently represents a cyano, carbamoyl, alkoxy carbonyl, alkylsulfonyl or arylsulfonyl group, R^{39} represents a hydrogen atom or a substituent, u stands for an integer of
15 from 0 to 4 and Z_4 represents $-\text{SO}_2-$ or $-\text{SO}-$, or salt thereof.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a hair dye
20 composition capable of dyeing the hair strongly into a vivid color tone without causing decomposition of the dye during the dyeing process, and exhibiting an excellent resistance against sunlight, hair washing, perspiration, friction and heat, having a high stability against an
25 alkali agent and an oxidizing agent, having high dyeing

properties, and not fading away easily even after passage of time; and a hair dyeing method using the composition.

The dissociative direct dye of formula (1) used in the present invention has a phenolic hydroxyl group or a sulfonamide group $\text{-NHSO}_2\text{R}^5$. At a certain pH or greater, proton dissociation occurs in the dye, which causes a change in color hue, thereby imparting a desired color hue to the hair. The dissociative direct dye (1) preferably does not contain, in the molecule thereof, a group which dissociates at a neutral pH such as carboxyl group, sulfo group or quaternary ammonium group.

In formula (1), examples of the substituent represented by R^1 , R^2 , R^3 , or R^4 include halogen atoms, alkyl groups, alkenyl groups, alkynyl groups, aryl groups, heterocyclic groups, a cyano group, a hydroxy group, a nitro group, a carboxyl group, alkoxy groups, aryloxy groups, silyloxy groups, heterocyclic oxy groups, acyloxy groups, carbamoyloxy groups, alkoxycarbonyloxy groups, aryloxy carbonyloxy groups, an amino group, alkylamino groups, arylamino groups, heterocyclic amino groups, acylamino groups, ureido groups, alkoxycarbonylamino groups, aryloxy carbonylamino groups, sulfamoylamino groups, alkylsulfonylamino groups, arylsulfonylamino groups, a mercapto group, alkylthio groups, arylthio groups, heterocyclic thio groups, sulfamoyl groups, a sulfo group,

alkylsulfinyl groups, arylsulfinyl groups, alkylsulfonyl groups, arylsulfonyl groups, acyl groups, alkoxycarbonyl groups, aryloxy carbonyl groups, carbamoyl groups, arylazo groups, heterocyclic azo groups, phosphino groups, phosphinyl groups, phosphinyloxy groups, phosphinylamino groups and silyl groups. When these substituents are further substitutable, they may have one or more substituents.

Specific examples of the above-described substituents (including the case where they are substituted further) will next be described.

The halogen atoms include fluorine, chlorine, bromine and iodine atoms.

The alkyl groups include linear, branched or cyclic C₁₋₁₀, preferably C₁₋₆ alkyl groups such as methyl, ethyl, n-propyl, isopropyl, t-butyl, n-octyl, 2-chloroethyl, 2-cyanoethyl, 2-ethylhexyl, cyclopropyl and cyclopentyl.

The alkenyl groups include linear, branched or cyclic C₂₋₁₀, preferably C₂₋₆ alkenyl groups such as vinyl, allyl, prenyl and cyclopenten-1-yl.

The alkynyl groups include C₂₋₁₀, preferably C₂₋₆ alkynyl groups such as ethynyl and propargyl.

The aryl groups include C₆₋₁₂, preferably C₆₋₈ aryl groups such as phenyl, p-tolyl, naphthyl, 3-chlorophenyl and 2-aminophenyl.

The heterocyclic groups include aromatic or nonaromatic, monovalent C₁₋₁₂, preferably C₂₋₆ groups obtained by removing one hydrogen atom from 5- or 6-membered heterocyclic compounds, such as 1-pyrazolyl, 1-imidazolyl, 2-furyl, 2-thienyl, 2-thiazolyl, benzothiazol-2-yl, isothiazol-5-yl, benzoisothiazol-7-yl, oxazol-2-yl, benzoxazol-2-yl, 1,2,4-thiadiazol-5-yl, 1,3,4-thiadiazol-2-yl, 1,2,4-oxadiazol-5-yl, 1,3,4-oxadiazol-2-yl, 1,2,4-triazol-3-yl, 4-pyridyl, 3-pyridyl, 4-pyrimidinyl and qunazolin-4-yl.

The alkoxy groups include linear, branched or cyclic, C₁₋₁₀, preferably C₁₋₆ alkoxy groups such as methoxy, ethoxy, isopropoxy, t-butoxy, cyclopentyloxy, 2-buten-1-yloxy and 2-methoxyethoxy.

The aryloxy groups include C₆₋₁₂, preferably C₆₋₈ aryloxy groups such as phenoxy, 2-methylphenoxy, 4-t-butylphenoxy and 3-nitrophenoxy.

The silyloxy groups include C₃₋₁₀, preferably C₃₋₆ silyloxy groups such as trimethylsilyloxy and t-butylldimethylsilyloxy.

The heterocyclic oxy groups include C₁₋₁₂, preferably C₂₋₆ heterocyclic oxy groups such as 1-phenyltetrazol-5-oxy and 2-tetrahydropyranyloxy.

The acyloxy groups include C₁₋₁₂, preferably C₁₋₈ acyloxy groups such as formyloxy, acetyloxy, pivaloyloxy,

benzoyloxy and p-methoxyphenylcarbonyloxy.

The carbamoyloxy groups include C₁₋₁₀, preferably C₁₋₆ carbamoyloxy groups such as N,N-dimethylcarbamoyloxy, N,N-diethylcarbamoyloxy, morpholinocarbonyloxy, and N-n-octylcarbamoyloxy.

The alkoxycarbonyloxy groups include C₂₋₁₀, preferably C₂₋₆ alkoxycarbonyloxy groups such as methoxycarbonyloxy, ethoxycarbonyloxy, t-butoxycarbonyloxy and n-octyloxy carbonyloxy.

The aryloxy carbonyloxy groups include C₇₋₁₂, preferably C₇₋₁₀ aryloxy carbonyloxy groups such as phenoxycarbonyloxy and p-methoxyphenoxycarbonyloxy.

The alkylamino groups include C₁₋₁₀, preferably C₁₋₆ alkylamino groups such as methylamino and dimethylamino.

The arylamino groups include C₆₋₁₂, preferably C₆₋₈ arylamino groups such as anilino, N-methylanilino and diphenylamino).

The heterocyclic amino groups include C₁₋₁₂, preferably C₂₋₆ heterocyclic amino groups such as imidazol-2-ylamino and pyrazol-3-ylamino.

The acylamino groups include C₁₋₁₀, preferably C₁₋₆ alkylcarbonylamino groups such as formylamino, acetylamino, and pivaloylamino, C₆₋₁₂, preferably C₆₋₈ arylcarbonylamino groups such as benzoylamino, C₂₋₁₂, preferably C₂₋₆ heterocyclic carbonylamino groups such as pyridine-4-

carbonylamino, thiophene-2-carbonylamino and morpholinocarbonylamino, and C₂₋₁₀, preferably C₄₋₈ imido groups such as N-succinimido and N-phthalimido.

5 The ureido groups include C₁₋₁₂, preferably C₁₋₆ ureido groups such as carbamoylamino, N,N-dimethylureido and N,N-diethylureido.

10 The alkoxy carbonylamino groups include C₂₋₁₀, preferably C₂₋₆ alkoxy carbonylamino groups such as methoxy carbonylamino, ethoxy carbonylamino and t-butoxy carbonylamino.

The aryloxy carbonylamino groups include C₇₋₁₂, preferably C₇₋₉ aryloxy carbonylamino groups such as phenoxy carbonylamino, p-chlorophenoxy carbonylamino and 4-methoxyphenoxy carbonylamino.

15 The sulfamoylamino groups include C₀₋₁₀, preferably C₀₋₆ sulfamoylamino groups such as sulfamoylamino, N,N-dimethylaminosulfonylamino and N-(2-hydroxyethyl)sulfamoylamino.

20 The alkylsulfonylamino groups include C₁₋₁₀, preferably C₁₋₆ alkylsulfonylamino groups such as methylsulfonylamino and butylsulfonylamino.

25 The arylsulfonylamino groups include C₆₋₁₂, preferably C₆₋₈ arylsulfonylamino groups such as phenylsulfonylamino, 2,3,5-trichlorophenylsulfonylamino and p-methylphenylsulfonylamino.

The alkylthio groups include C₁₋₁₀, preferably C₁₋₆ alkylthio groups such as methylthio, ethylthio and butylthio.

5 The arylthio groups include C₆₋₁₂, preferably C₆₋₈ arylthio groups such as phenylthio, p-chlorophenylthio and m-methoxyphenylthio.

The heterocyclic thio groups include C₂₋₁₀, preferably C₂₋₆ heterocyclic thio groups such as 2-benzothiazolylthio and 1-phenyltetrazol-5-ylthio.

10 The sulfamoyl groups include C₀₋₁₀, preferably C₀₋₆ sulfamoyl groups such as sulfamoyl, N-ethylsulfamoyl, N,N-dimethylsulfamoyl, N-acetylsulfamoyl and N-benzoylsulfamoyl.

15 The alkylsulfinyl groups include C₁₋₁₀, preferably C₁₋₆ alkylsulfinyl groups such as methylsulfinyl and ethylsulfinyl.

The arylsulfinyl groups include C₆₋₁₂, preferably C₆₋₈ arylsulfinyl groups such as phenylsulfinyl and p-methylphenylsulfinyl.

20 The alkylsulfonyl groups include C₁₋₁₀, preferably C₁₋₆ alkylsulfonyl groups such as methylsulfonyl and ethylsulfonyl.

The arylsulfonyl groups include C₆₋₁₂, preferably C₆₋₈ arylsulfonyl groups such as phenylsulfonyl and p-chlorophenylsulfonyl.

25 The acyl groups include formyl group, C₂₋₁₀,

preferably C₂₋₆ alkylcarbonyl groups such as acetyl, pivaloyl and 2-chloroacetyl, and C₇₋₁₂, preferably C₇₋₉ arylcarbonyl groups such as benzoyl and 2,4-dichlorobenzoyl.

5 The alkoxycarbonyl groups include C₂₋₁₀, preferably C₂₋₆ alkoxycarbonyl groups such as methoxycarbonyl, ethoxycarbonyl, t-butoxycarbonyl and isobutoxycarbonyl.

10 The aryloxy carbonyl groups include C₇₋₁₂, preferably C₇₋₉ aryloxy carbonyl groups such as phenoxycarbonyl, 2-chlorophenoxycarbonyl, 3-nitrophenoxycarbonyl and 4-t-butylphenoxycarbonyl.

The carbamoyl groups include C₁₋₁₀, preferably C₁₋₆ carbamoyl groups such as carbamoyl, N-methylcarbamoyl, N,N-dimethylcarbamoyl, N-(2-hydroxyethyl)carbamoyl and N-(methylsulfonyl)carbamoyl.

15 The arylazo groups include C₆₋₁₂, preferably C₆₋₈ arylazo groups such as phenylazo and p-chlorophenylazo.

The heterocyclic azo groups include C₁₋₁₀, preferably C₁₋₆ heterocyclic azo groups such as pyrazol-3-ylazo, thiazol-2-ylazo, 5-ethylthio-1,3,4-thiadiazol-2-ylazo.

20 The phosphino groups include C₂₋₁₂, preferably C₂₋₆ phosphino groups such as dimethylphosphino, diphenylphosphino and methylphenoxyphosphino.

The phosphinyl groups include C₂₋₁₂, preferably C₂₋₆ phosphinyl groups such as phosphinyl and diethoxyphosphinyl.

25 The phosphinyloxy groups include C₂₋₁₂, preferably C₂₋₆

phosphinyloxy groups such as diphenoxyphosphinyloxy and dibutoxyphosphinyloxy.

The phosphinylamino groups include C₂₋₁₂, preferably C₂₋₆ phosphinylamino groups such as dimethoxyphosphinylamino and dimethylaminophosphinylamino.

The silyl groups include C₃₋₁₂, preferably C₃₋₈ silyl groups such as trimethylsilyl, t-butyl dimethylsilyl and phenyl dimethylsilyl.

When the above-described substituents R¹, R², R³ and R⁴ are further substitutable, they may have one or more substituents. In such a case, preferable substituents are the same substituent groups as described above and a preferable range of the total number of the carbon atoms of R¹, R², R³ and R⁴ does not exceed the above-described range. When they have two or more substituents, the substituents may be the same or different.

In -NHSO₂R⁵ represented by X in formula (1), the preferable number of carbon atoms of the alkyl group, aryl group or heterocyclic group represented by R⁵ and specific examples of the group are the same as those described above in the substituents represented by R¹ to R⁴.

In the group represented by A, that is, a group represented by any one of formulas (Cp-1) through (Cp-12) in formula (1), the preferable number of carbon atoms of the group represented by R¹¹ to R³⁹ and R¹⁰¹ to R¹⁰³ and

specific examples of the group are the same as those described above in the substituents represented by R^1 to R^4 , with the proviso that at least one of R^{102} and R^{103} is an electron attractive group having a Hammett σ_p value of 0.1 or greater, preferably 0.2 or greater. Examples of the electron attractive group having a Hammett σ_p value of 0.1 or greater include a chlorine, bromine or iodine atom, or an alkoxycarbonyl, carbamoyl, alkylaminocarbonyl, dialkylaminocarbonyl, sulfamoyl, alkylaminosulfonyl, dialkylaminosulfonyl or acyl group. The Hammett empirical rule was advocated by L.P. Hammett in 1935 in order to quantitatively discuss the influence of a substituent on the reaction or equilibrium of a benzene derivative and its validity is now recognized widely. The substituent constants determined by the Hammett rule are σ_p and σ_m values. These values are found generally in many books and described in detail, for example, in *Lange's Handbook of Chemistry*, 12 ed., 1979, ed. J.A. Dean, (published by McGraw-Hill), *Journal of Japanese Chemistry*, Extra Number, 122, 96-103(1979) (published by Nankodo) and *Chemical Review*, 91, 165-195(1991).

The preferable range of dissociative direct dye (1) will next be described.

As R^1 or R^2 in formula (1), preferred are a hydrogen atom, halogen atoms, alkyl groups, a cyano group, acylamino

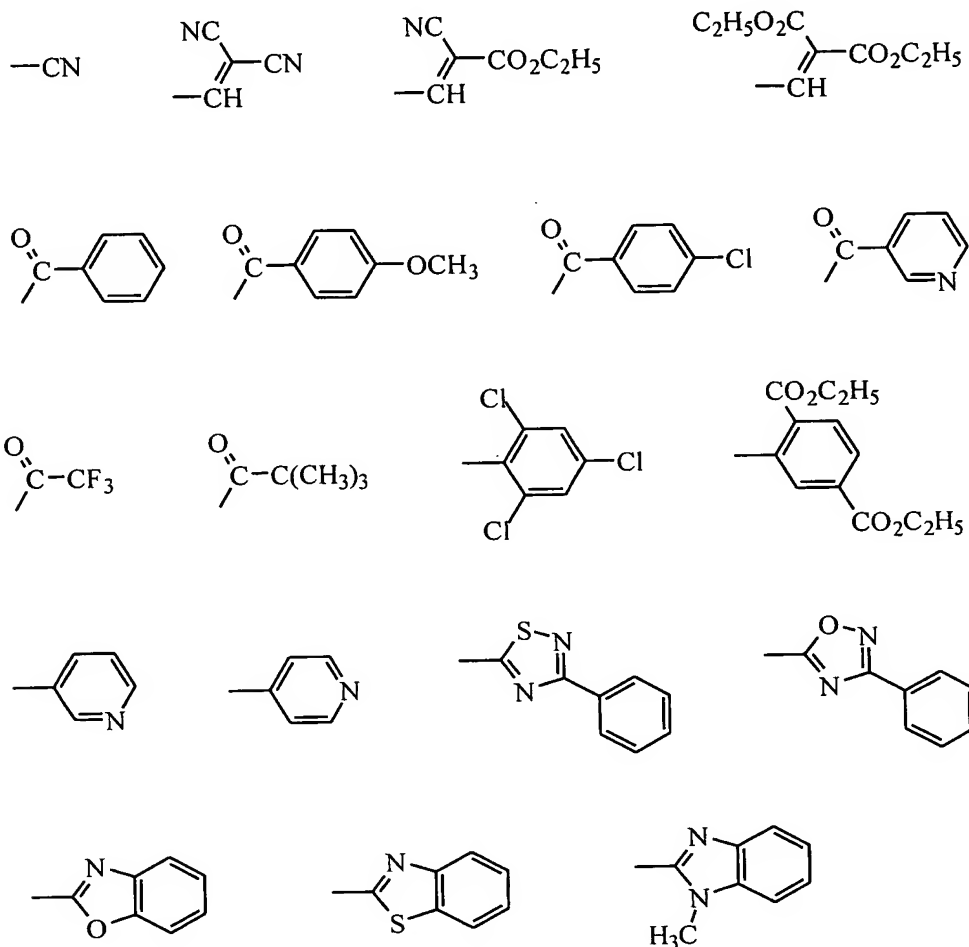
groups, ureido groups, alkoxycarbonylamino groups, aryloxy carbonylamino groups, sulfamoylamino groups, alkylsulfonylamino groups, arylsulfonylamino groups, alkoxycarbonyl groups, sulfamoyl groups and carbamoyl groups, of which a hydrogen atom, a chlorine atom, a bromine atom, alkyl groups, a cyano group, acylamino groups, ureido groups, alkoxycarbonylamino groups, alkylsulfonylamino groups, arylsulfonylamino groups and carbamoyl groups are more preferred, with hydrogen and chlorine atoms and acylamino and carbamoyl groups being most preferred.

As R^3 or R^4 in formula (1), preferred are a hydrogen atom, halogen atoms, alkyl groups and acylamino groups, of which a hydrogen atom, chlorine atom and alkyl groups are more preferred, with a hydrogen atom being most preferred.

As X in formula (1), a hydroxyl group is more preferred. When X represents $-NHSO_2R^5$, R^5 preferably represents an alkyl group.

As A in formula (1), the below-described groups are preferred.

In formula (Cp-1), preferred as R^{11} are a cyano group, acyl groups, heterocyclic groups and $-C(R^{101})=C(R^{102})-R^{103}$, with the following groups being particularly preferred.



In formula (Cp-2), preferred as R¹² are a cyano group, aryl groups and heterocyclic groups. The cyano group and heterocyclic groups exemplified above as particularly preferred specific examples as R¹¹ are also preferred as R¹².
 5 As R¹³ and R¹⁴, a hydrogen atom, alkyl groups and aryl groups are preferred. It is preferred that at least one of R¹³ and R¹⁴ represents a hydrogen atom.

In formula (Cp-3), preferred as R¹⁵ are alkyl groups, amino group, alkylamino groups, arylamino groups, heterocyclic amino groups, alkoxy groups, acylamino groups,
 10

alkoxycarbonylamino groups, ureido group, alkoxycarbonyl groups, carbamoyl groups and a cyano group, of which alkyl groups, acylamino groups, alkoxycarbonyl groups and a cyano group are more preferred. As R^{16} , aryl groups and
5 heterocyclic groups are preferred, with aryl groups being most preferred.

In formula (Cp-4), preferred as R^{17} and R^{18} are alkyl groups and aryl groups.

In formula (Cp-5), preferred as R^{19} and R^{20} are aryl
10 groups and heterocyclic groups, with aryl groups being most preferred.

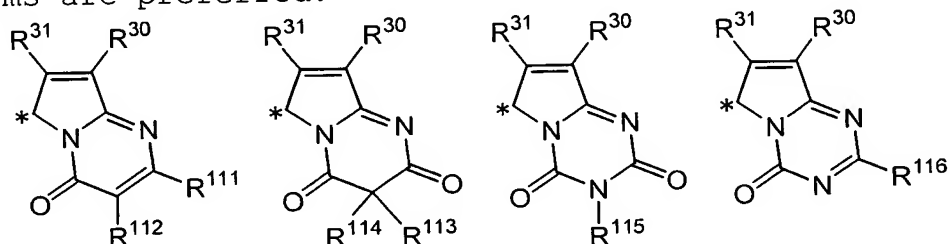
In formula (Cp-6), preferred as R^{21} and R^{22} are a cyano group, carbamoyl groups and alkoxycarbonyl groups, of which a cyano group and alkoxycarbonyl groups are more
15 preferred. As R^{23} , a hydrogen atom and alkyl groups are preferred.

In formula (Cp-7), preferred as R^{24} are hydrogen atom, aryl groups, acylamino groups, alkylsulfonylamino groups and arylsulfonylamino groups. As R^{25} and R^{26} , a hydrogen
20 atom, aryl groups, alkoxycarbonyl groups, carbamoyl groups, alkylsulfonyl groups, arylsulfonyl groups and a cyano group are preferred, with aryl groups, alkoxycarbonyl groups, carbamoyl groups and a cyano group being more preferred.

In formula (Cp-8), preferred as R^{27} and R^{28} are a
25 cyano group, carbamoyl groups and alkoxycarbonyl groups,

while as R^{29} , halogen atoms, acylamino groups,
alkylsulfonylamino groups, arylsulfonylamino groups,
alkoxycarbonyl groups, carbamoyl groups, alkylsulfonyl
groups and arylsulfonyl groups are preferred. As s, an
integer of from 0 to 2 is preferred.

In formula (Cp-9), preferred as R^{30} and R^{31} are a
hydrogen atom, alkyl groups, aryl groups, heterocyclic
groups, alkoxycarbonyl groups, carbamoyl groups,
alkylsulfonyl groups, arylsulfonyl groups and a cyano group,
of which alkyl groups, aryl groups, alkoxycarbonyl groups,
carbamoyl groups and a cyano group are more preferred. As
 Z^1 , groups capable of forming the below-described ring
systems are preferred.

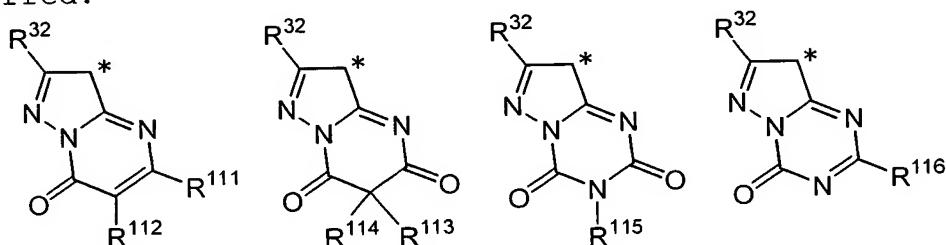


wherein, R^{111} represents a hydrogen atom or an alkoxy, amino,
alkylamino, arylamino, heterocyclic amino, acylamino,
ureido, alkoxycarbonylamino, aryloxycarbonylamino,
sulfamoylamino, alkylsulfonylamino, arylsulfonylamino,
alkylthio, arylthio or heterocyclic thio group, R^{112}
represents a hydrogen or halogen atom, or an alkyl, acyl,
carbamoyl or alkoxycarbonyl group, R^{113} and R^{114} each
independently represents a hydrogen atom or an alkyl group,

R^{115} represents a hydrogen atom or an alkyl group, and R^{116} represents a hydrogen atom or an alkyl, aryl, alkoxy, aryloxy, amino, alkylamino, arylamino, heterocyclic amino, acylamino, ureido, alkoxycarbonylamino, alkylsulfonylamino, arylsulfonylamino, alkylthio or arylthio group.

The preferable number of the carbon atoms of R^{111} to R^{116} and specific examples thereof are similar to those described above for the substituents represented by R^1 to R^4 .

In formula (Cp-10), preferred as R^{32} are hydrogen atom, alkyl groups, aryl groups, heterocyclic groups, alkoxycarbonyl groups, carbamoyl groups, alkylsulfonyl groups, arylsulfonyl groups and a cyano group, of which alkyl groups, aryl groups, alkoxycarbonyl groups, carbamoyl groups and a cyano group are more preferred. As Z^2 , groups capable of forming the below-described ring systems are preferred.



wherein, R^{111} to R^{116} have the same meanings as described above.

In formula (Cp-11), Z^3 preferably represents $-C(R^{36})=$, and preferred are the case where R^{36} is a hydrogen

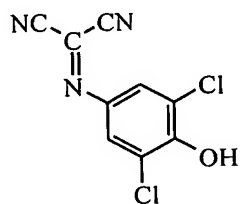
atom or an acylamino group, R^{33} and R^{34} each represents a hydrogen atom, a halogen atom, an alkyl group or acylamino group, and R^{35} represents a hydrogen atom or an alkyl group, and the case where R^{34} and R^{36} are coupled together to form
5 a benzene ring which may be substituted with a halogen atom or an amino, alkylamino, arylamino, heterocyclic amino, acylamino, ureido, alkoxycarbonylamino, alkylsulfonylamino or arylsulfonylamino group, R^{33} represents an acylamino, alkylsulfonylamino, arylsulfonylamino, carbamoylamino or
10 sulfamoyl group, and R^{35} represents a hydrogen atom.

In formula (Cp-12), preferred as R^{37} and R^{38} are a cyano group and alkoxycarbonyl groups, preferred as R^{39} are halogen atoms, acylamino groups, alkylsulfonylamino groups, arylsulfonylamino groups, alkoxycarbonyl groups, carbamoyl
15 groups, alkylsulfonyl groups and arylsulfonyl groups, preferred as u is an integer of from 0 to 2, and preferred as Z^4 is $-SO_2-$.

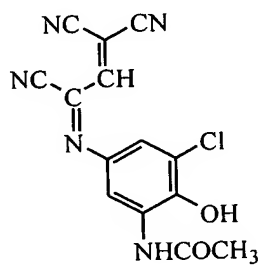
Among the dissociative direct dyes (1), those having as A the group of formula (Cp-1), (Cp-2), (Cp-3), (Cp-4),
20 (Cp-7), (Cp-9) or (Cp-11) are more preferred, of which those having as A the group of formula (Cp-1), (Cp-2), (Cp-3) or (Cp-11) are particularly preferred.

Preferable specific examples of the dissociative direct dye (1) will be shown below.

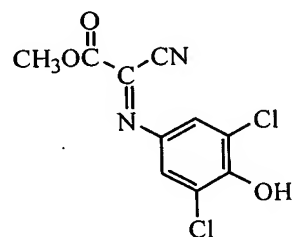
D-1



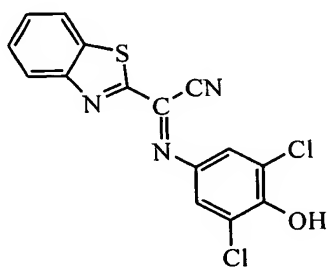
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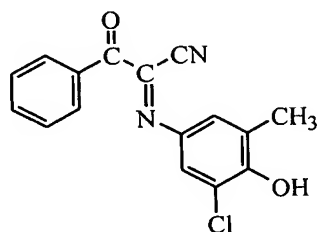
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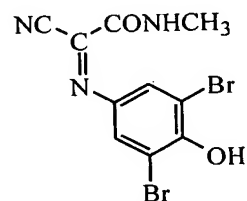
D-4



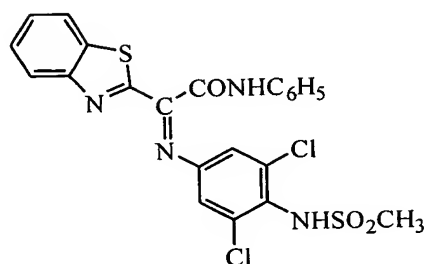
D-5



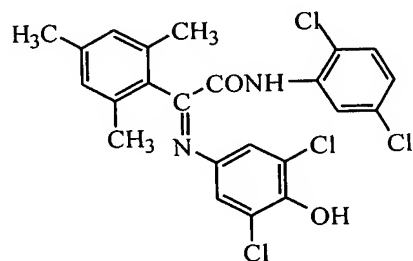
D-6



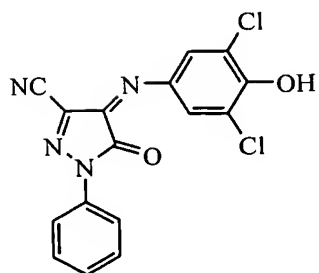
D-7



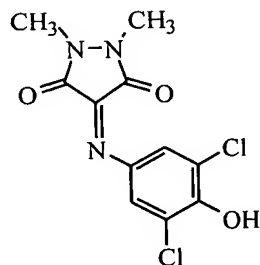
D-8



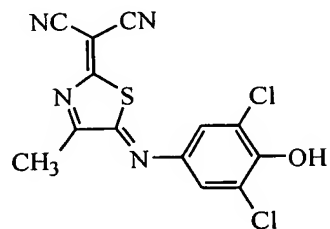
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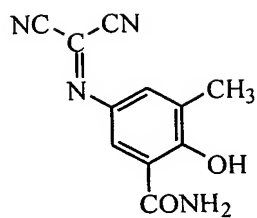
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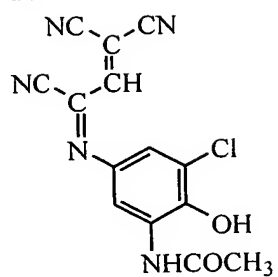
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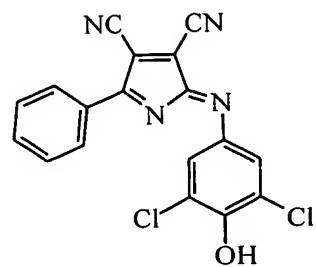
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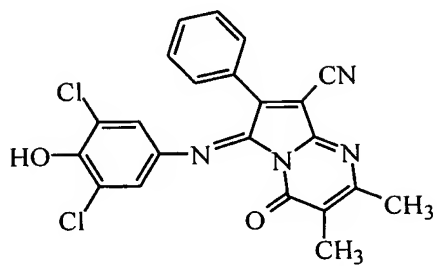
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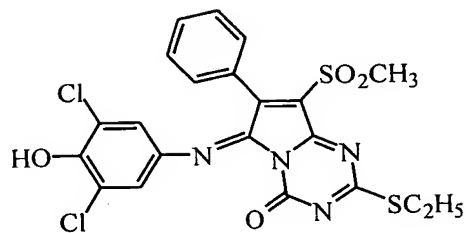
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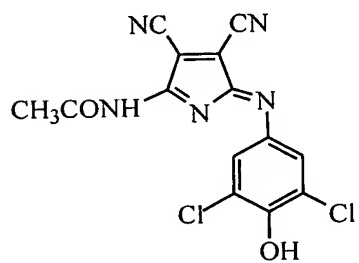
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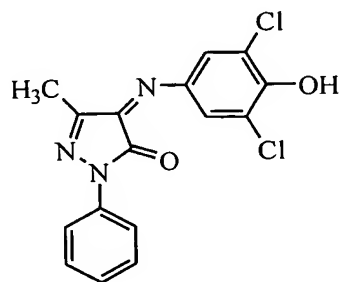
D-16



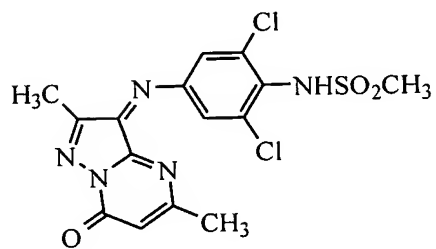
D-17



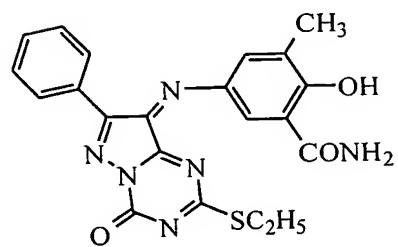
D-18



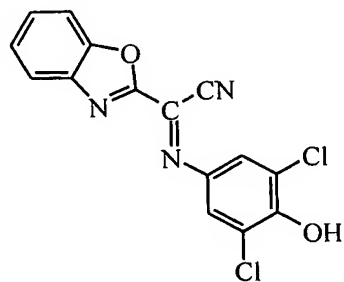
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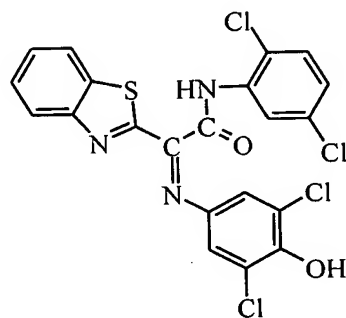
D-20



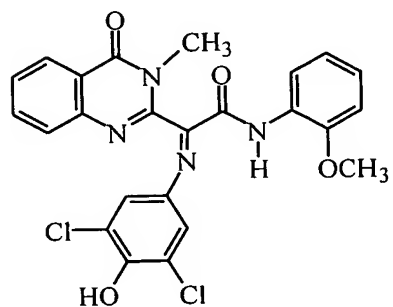
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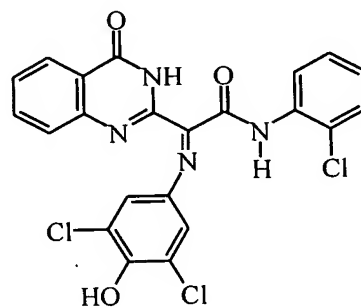
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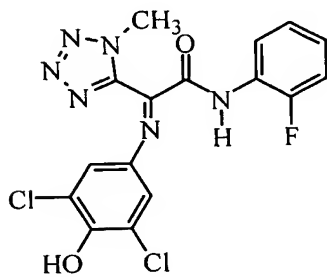
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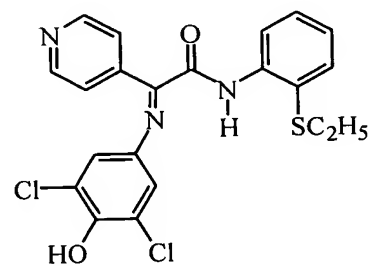
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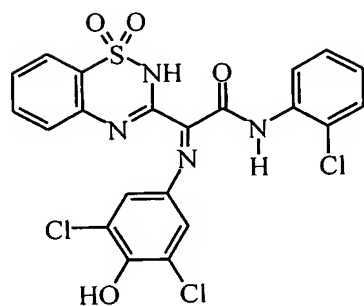
D-25



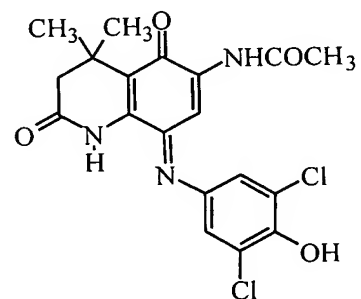
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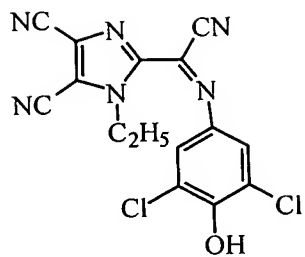
D-27



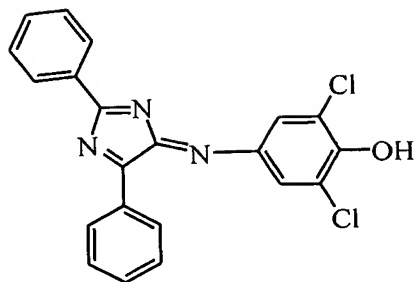
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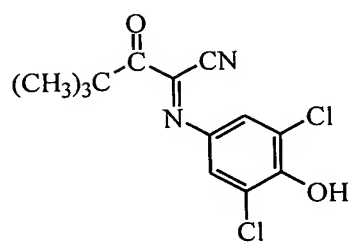
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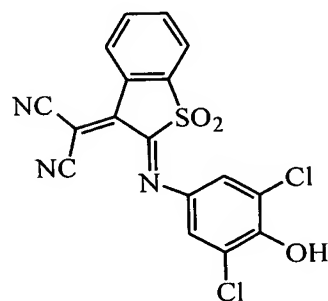
D-30



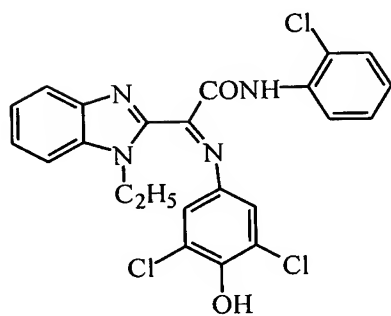
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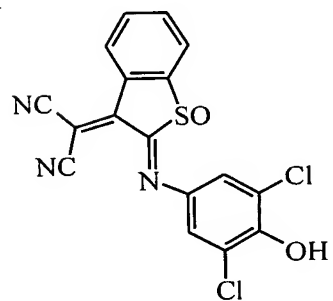
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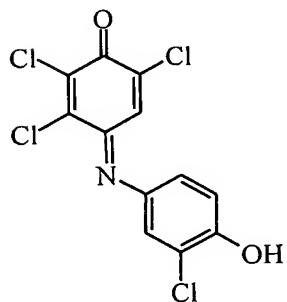
D-33



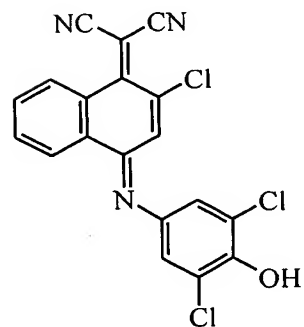
D-34



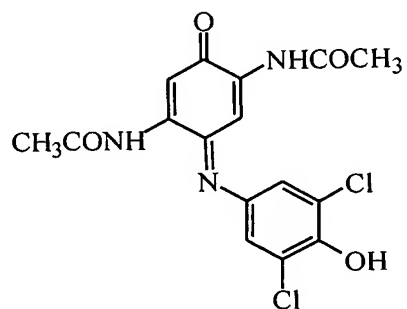
D-35



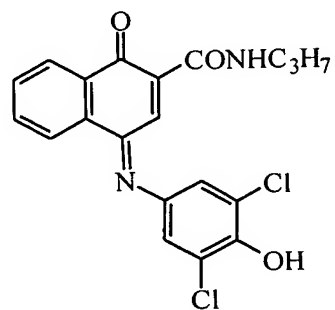
D-36



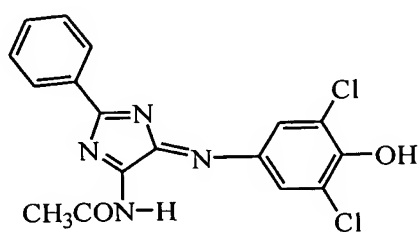
D-37



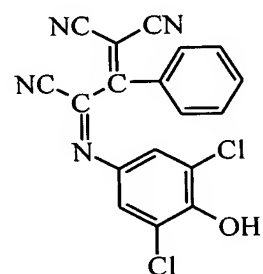
D-38



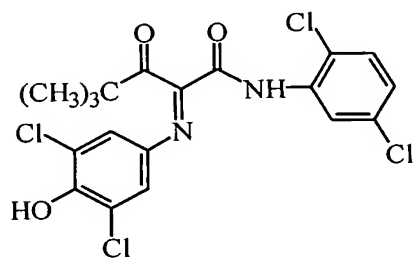
D-39



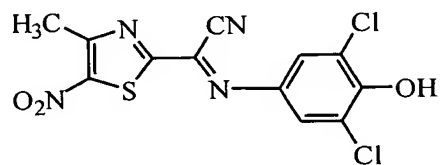
D-40



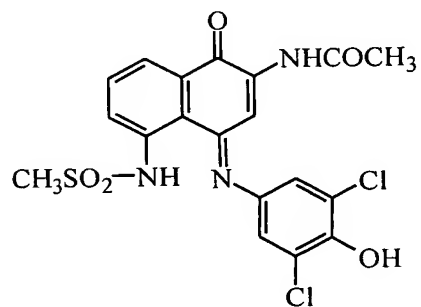
D-41



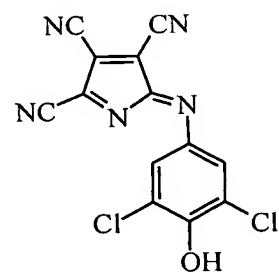
D-42



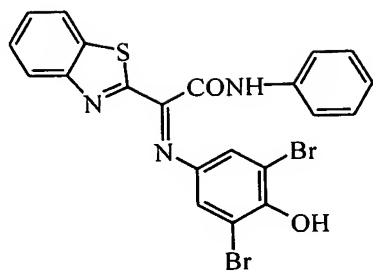
D-43



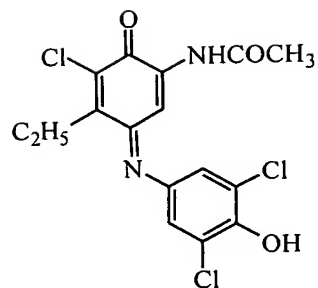
D-44



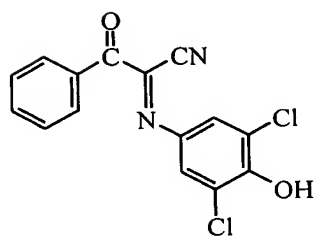
D-45



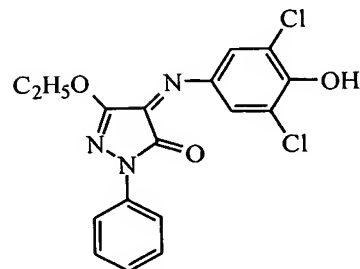
D-46



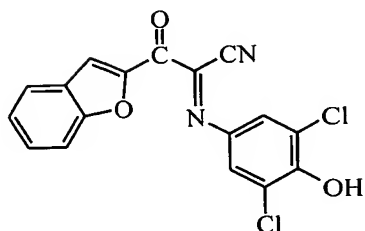
D-47



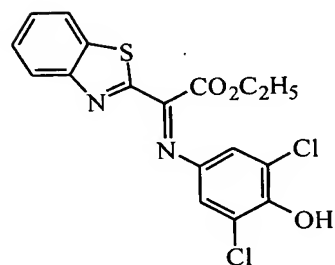
D-48



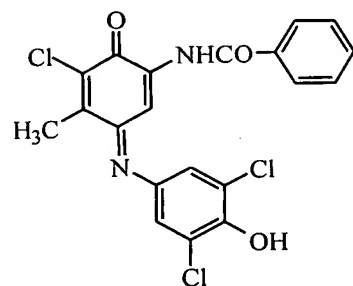
D-48



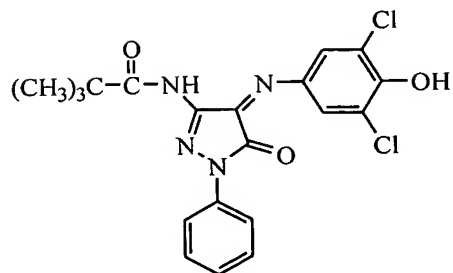
D-49



D-50



D-51

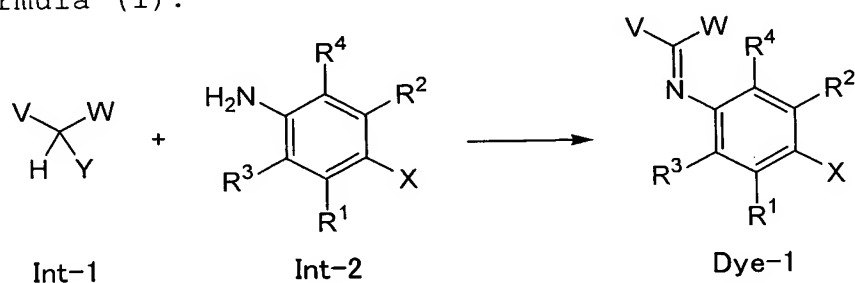


The dissociative direct dye (1) may be a salt of an

organic or inorganic acid, or a salt of an organic or inorganic alkali. Examples of the organic or inorganic acid include hydrochloric acid, sulfuric acid, phosphoric acid, acetic acid, propionic acid, lactic acid and citric acid, while those of the organic or inorganic alkali include ammonium hydroxide, 2-ethanolammonium hydroxide, sodium hydroxide and potassium hydroxide.

The dissociative direct dye (1) can be synthesized in accordance with the below-described reaction scheme.

Specifically, Dye-1, which is a dissociative direct dye (1), is available by condensing Int-1 (wherein, Y represents a hydrogen atom, a halogen atom or a group capable of being dissociated as an anion) which is a coupler compound and Int-2, which is a p-aminophenol (or p-sulfonamidoaniline) derivative, in the presence of a base and an oxidizing agent. In the below-described scheme, V-C-W corresponds to A in formula (1).



A coupler compound such as Int-1 can be synthesized in accordance with a process as described in the literature on a coupler in the field of silver halide color photosensitive materials. Specifically, the process as

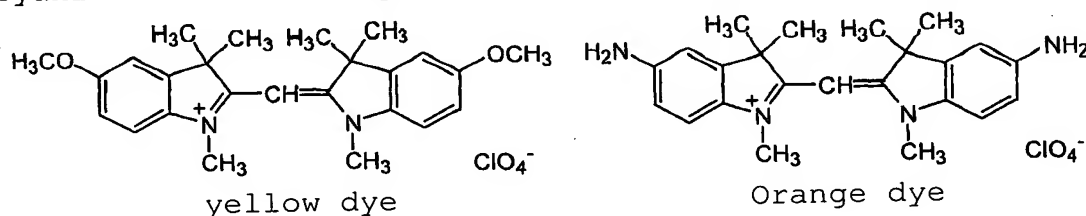
described in the literature cited on pp. 613 to 617 of Research Disclosure 40145 (September, 1997), or the process as described on pp. 80 to 83 of Research Disclosure 37038 (February, 1995) can be adopted.

5 The pKa of the dissociative direct dye (1) is preferably from 1.5 to 9, especially preferably from 2 to 8, most preferably from 2 to 7.5, from the viewpoint of hair coloring performance and color retention attained by the dye. The pKa value can be determined in the following
10 manner. First, a sample is dissolved in a 1:1 (volume ratio) solution of DMF and water to give its final concentration of 2×10^{-5} mol/L. After adjustment of the pH of the resulting solution to 2 with 1.0 mol/L hydrochloric acid, the solution was titrated with a 1.0 mol/L aqueous
15 solution of sodium hydroxide. Variations in a visible ultraviolet absorption spectrum is recorded and an inflection point is determined by regression analysis.

 In the hair dye composition of the present invention, the dissociative direct dye (1) can be used in combination
20 with another direct dye or an oxidation dye.

 Examples of such a direct dye include Basic Blue 7 (C.I. 42595), Basic Blue 26 (C.I. 44045), Basic Blue 99 (C.I. 56059), Basic Violet 10 (C.I. 45170), Basic Violet 14 (C.I. 42515), Basic Brown 16 (C.I. 12250), Basic Brown 17
25 (C.I. 12251), Basic Red 2 (C.I. 50240), Basic Red 12 (C.I.

48070), Basic Red 22 (C.I. 11055), Basic Red 46 (C.I. 110825), Basic Red 76 (C.I. 12245), Basic Red 118 (C.I. 12251:1), Basic Yellow 28 (C.I. 48054) and Basic Yellow 57 (C.I. 12719); cationic dyes as described in Japanese Patent
 5 Laid-Open Nos. 2204/1983 and 118832/1997, and Japanese Language Laid-Open Publications (PCT) Nos. 501322/1996 and 507545/1996; and methine type cationic dyes having a cyanine structure represented by the following formulas:



10 The dissociative direct dye (1) is added preferably in an amount of 0.0001 to 20 wt.%, more preferably 0.001 to 20 wt.%, more preferably from 0.05 to 10 wt.%, especially preferably from 0.1 to 5 wt.% based on the whole composition (after mixing of all the component parts when
 15 the composition is a two part or three part composition; this will be applied equally hereinafter). When another direct dye is used in combination, the total content of the dissociative direct dye (1) and the another direct dye preferably ranges from 0.001 to 20 wt.%, more preferably
 20 from 0.01 to 20 wt.%, still more preferably from 0.05 to 10 wt.%, especially preferably from 0.1 to 5 wt.%.

In the hair dye composition of the present invention, the dissociative direct dye (1) exhibits a high storage

stability within a wide pH range from 2 to 11 which is a pH range employed ordinarily for hair dyes, so that the hair dye composition of the present invention can be used at any pH in the above-described pH range. Use in a pH range of from 5 or greater is however preferred from the viewpoint of dyeing property. Moreover, owing to the high stability of the dissociative direct dye (1) against an alkali agent, the hair dye composition of the present invention can be used at a pH 8 or greater, particularly 8 to 11 which permits the composition to exhibit a high dyeing property, so that even after long storage, a high dyeing property can be kept without causing decomposition of the direct dye.

Examples of the alkali agent used for the hair dye composition of the present invention include ammonia, alkanolamines such as monoethanolamine and isopropanolamine or salts thereof, guanidium salts such as guanidine carbonate, and hydroxides such as sodium hydroxide. The alkali agent is added preferably in an amount of from 0.01 to 20 wt.%, more preferably 0.1 to 10 wt.%, especially preferably 0.5 to 5 wt.% based on the whole composition.

Since the dissociative direct dye (1) has a high stability against an oxidizing agent, it can be applied to the hair after mixing with an oxidizing agent. In other words, it can be provided as a two-part composition composed of a first part containing the dissociative direct

dye (1) and a second part containing an oxidizing agent. In this case, hair dyeing and bleaching can be carried out simultaneously, which facilitates more vivid hair dyeing.

Examples of the oxidizing agent include hydrogen peroxide, persulfates such as ammonium persulfate, potassium persulfate and sodium persulfate, perborates such as sodium perborate, percarbonates such as sodium percarbonate and bromates such as sodium bromate and potassium bromate. Hydrogen peroxide is especially preferred from the viewpoints of hair bleaching property, stability and effectiveness of the dissociative direct dye (1). Hydrogen peroxide may be used in combination with another oxidizing agent. The oxidizing agent is added preferably in an amount of from 0.5 to 10 wt.%, especially preferably from 1 to 8 wt.%, based on the whole composition.

The first part containing the dissociative direct dye (1) and the second part containing the oxidizing agent are mixed at a volume ratio preferably ranging from 2:1 to 1:3.

In the hair dye composition of the present invention, an oxidation dye can be used in combination with the dissociative direct dye (1). Such combined use enables considerably vivid and intense dyeing which cannot be accomplished by the single use of the oxidation dye. For the oxidation dye, known developers and couplers ordinarily employed for an oxidation type hair dye can be used.

Examples of the developer include

paraphenylenediamine, toluene-2,5-diamine, 2-chloro-
 paraphenylenediamine, N-methoxyethyl-paraphenylenediamine,
 N,N-bis(2-hydroxyethyl)-paraphenylenediamine, 2-(2-
 5 hydroxyethyl)-paraphenylenediamine, 2,6-dimethyl-para-
 phenylenediamine, 4,4'-diaminodiphenylamine, 1,3-bis(N-(2-
 hydroxyethyl)-N-(4-aminophenyl)amino)-2-propanol, PEG-
 3,2,2'-paraphenylenediamine, paraaminophenol,
 paramethylaminophenol, 3-methyl-4-aminophenol, 2-
 10 aminomethyl-4-aminophenol, 2-(2-hydroxyethylaminomethyl)-4-
 aminophenol, orthoaminophenol, 2-amino-5-methylphenol, 2-
 amino-6-methylphenol, 2-amino-5-acetamidophenol, 3,4-
 diaminobenzoic acid, 5-aminosalicylic acid, 2,4,5,6-
 tetraaminopyrimidine, 2,5,6-triamino-4-hydroxypyrimidine
 15 and 4,5-diamino-1-(4'-chlorobenzyl)pyrazole and salts
 thereof.

Examples of the coupler include metaphenylenediamine,
 2,4-diaminophenoxyethanol, 2-amino-4-(2-
 hydroxyethylamino)anisole, 2,4-diamino-5-methylphenetole,
 20 2,4-diamino-5-(2-hydroxyethoxy)toluene, 2,4-dimethoxy-1,3-
 diaminobenzene, 2,6-bis(2-hydroxyethylamino)toluene, 2,4-
 diamino-5-fluorotoluene, 1,3-bis(2,4-diaminophenoxy)propane,
 metaaminophenol, 2-methyl-5-aminophenol, 2-methyl-5-(2-
 hydroxyethylamino)phenol, 2,4-dichloro-3-aminophenol, 2-
 25 chloro-3-amino-6-methylphenol, 2-methyl-4-chloro-5-

aminophenol, N-cyclopentyl-metaaminophenol, 2-methyl-4-methoxy-5-(2-hydroxyethylamino)phenol, 2-methyl-4-fluoro-5-aminophenol, resorcin, 2-methylresorcin, 4-chlororesorcin, 1-naphthol, 1,5-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 2-isopropyl-5-methylphenol, 4-hydroxyindole, 5-hydroxyindole, 6-hydroxyindole, 7-hydroxyindole, 6-hydroxybenzomorpholine, 3,4-methylenedioxyphenol, 2-bromo-4,5-methylenedioxyphenol, 3,4-methylenedioxyaniline, 1-(2-hydroxyethyl)amino-3,4-methylenedioxybenzene, 2,6-dihydroxy-3,4-dimethylpyridine, 2,6-dimethoxy-3,5-diaminopyridine, 2,3-diamino-6-methoxypyridine, 2-methylamino-3-amino-6-methoxypyridine, 2-amino-3-hydroxypyridine, and 2,6-diaminopyridine and salts thereof.

As each of the developer and coupler, at least two of the above-described developer or coupler are usable. The content of each of them is preferably from 0.01 to 20 wt.%, especially preferably from 0.5 to 10 wt.% based on the whole composition.

To the hair dye composition of the present invention, an autoxidation dye typified by an indole or an indoline, or a known direct dye such as a nitro dye or a disperse dye can also be added.

Addition of a polyol, polyol alkyl ether, cationic or amphoteric polymer or silicone to the hair dye composition

of the present invention is preferred, because the resulting composition can dye the hair uniformly and has improved cosmetic effects of the hair.

5 In addition to the above-described components, those ordinarily employed as a raw material for cosmetics can be added to the hair dye composition of the present invention. Examples of such an optional component include hydrocarbons, animal or vegetable fats and oils, higher fatty acids, organic solvents, penetration promoters, cationic
10 surfactants, natural or synthetic polymers, higher alcohols, ethers, amphoteric surfactants, nonionic surfactants, anionic surfactants, protein derivatives, amino acids, antiseptics, chelating agents, stabilizers, antioxidants, plant extracts, crude drug extracts, vitamins, colorants,
15 perfumes and ultraviolet absorbers.

The hair dye composition of the present invention can be prepared in a conventional manner to form a one-part composition, a two-part composition having a first part containing an alkali agent and a second part containing an
20 oxidizing agent, or a three-part composition having, in addition to these two parts, a powdery oxidizing agent such as persulfate. The direct dye (1) may be incorporated in at least one of these parts of the two-part or three-part composition. The direct dye (1) may be incorporated in at
25 least one of these parts of the two-part or three-part

composition. When the hair dye composition of the present invention is one-part type, it is applied to the hair directly, while when it is two- or three-part type, these parts are mixed upon hair dyeing and the mixture is applied to the hair.

In the case of preparation of the hair dye composition of the present invention as a two-part type, the first part is typically prepared by mixing the dissociative direct dye (1) and optionally an oxidation dye and adjusting the pH of the mixture to 8 to 12 with an alkali agent such as ammonia. The second part is prepared by incorporating about 2 to 6 wt.% of hydrogen peroxide, adjusting the mixture to weakly acidic with phosphoric acid. When the composition is a three-part type, a persulfate is mixed with an inert substance such as talc or dextrin and a bonding agent to convert the mixture into a granular substance containing about 5 to 95 wt.% of persulfate. The granular substance is added to a mixture of the first part and the second part upon use.

The hair dye composition of the present invention can be provided in the form of powder, transparent liquid, emulsion, cream, gel, paste, aerosol, aerosol foam or the like. It preferably has a viscosity of 2000 to 100000 mPa·s upon its application to the hair (after mixing of all the parts when the composition is a two-part or three-part

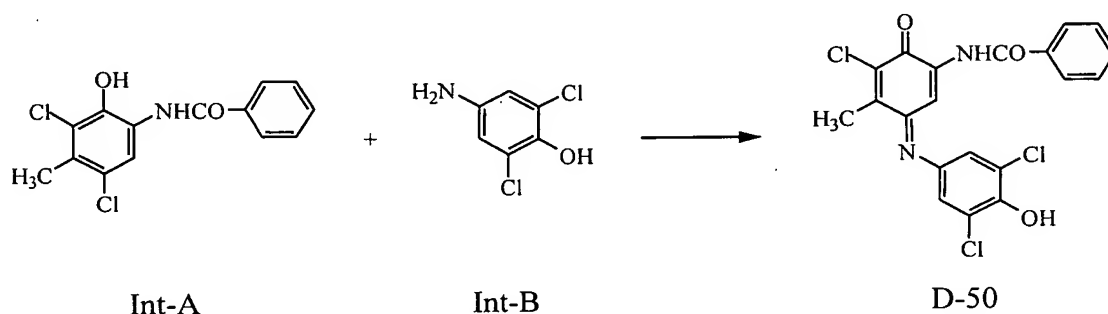
type). The above-described viscosity is measured at 20°C by using a Brookfield rotary viscometer (No. 5 spindle, 5 rpm).

-Examples-

5 The synthesis examples of the dissociative direct dye (1) will next be described specifically.

Synthesis Example 1 <Synthesis of Exemplified Compound D-50>

10 Synthesis was conducted in accordance with the following scheme.

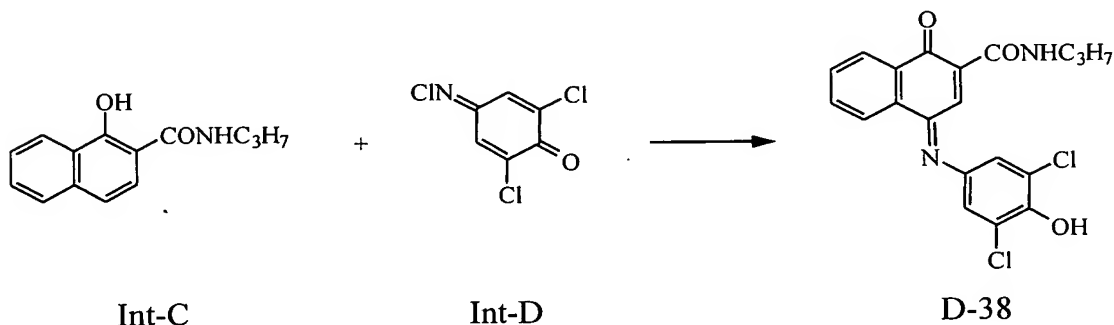


To 100 mL of ethyl acetate were added 2.96 g of N-(3,5-dichloro-2-hydroxy-4-methylphenyl)benzamide (Int-A), 2.10 g of commercially available 4-amino-2,6-dichlorophenol (Int-B), and 5.6 mL of triethylamine. The resulting mixture was stirred at room temperature. After addition of 3.5 g of silver acetate in several portions, stirring of the mixture was continued for 3 hours. The reaction mixture was filtered under reduced pressure. The cake on the Nutsche was added to 200 mL of acetone. The mixture was heated under reflux for 1 hour under stirring, followed

by hot filtration. To the filtrate was added 1 mL of concentrated hydrochloric acid and the mixture was concentrated under reduced pressure. To the residue were added acetonitrile and water to disperse the former in the latter. The crystals thus precipitated were collected by filtration. After washing while pouring water, the crystals thus obtained were air dried, whereby 2.47 g of Exemplified Compound D-50 was obtained as dark purple crystals (yield: 57%).

Synthesis Example 2 <Synthesis of Exemplified Compound D-38>

Synthesis was conducted in accordance with the following scheme.

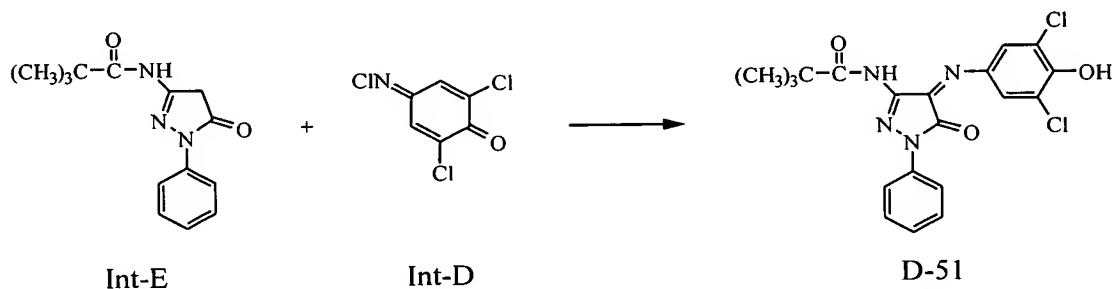


To 50 mL of ethyl acetate were added 2.37 g of N-propyl-1-hydroxy-2-naphthamide (Int-C) and 2.8 mL of triethylamine. The resulting mixture was stirred at room temperature. After addition of 2.20 g of commercially available 2,6-dichloroquinone-4-chloroimide (Int-D) in several portions, stirring was continued for 2 hours. To the reaction mixture were added 30 mL of acetonitrile and

dilute hydrochloric acid (obtained by diluting 1.9 mL of concentrated hydrochloric acid with 10 mL of water). The resulting mixture was stirred for 30 minutes. The crystals thus precipitated were filtered under reduced pressure and then washed while pouring thereon 50 mL of water and then 20 mL of acetonitrile. The crystals were air dried, whereby 2.5 g of Exemplified D-38 was obtained as dark red crystals (yield: 62%).

Synthesis Example 3 <Synthesis of Exemplified Compound D-51>

Synthesis was conducted in accordance with the following scheme:

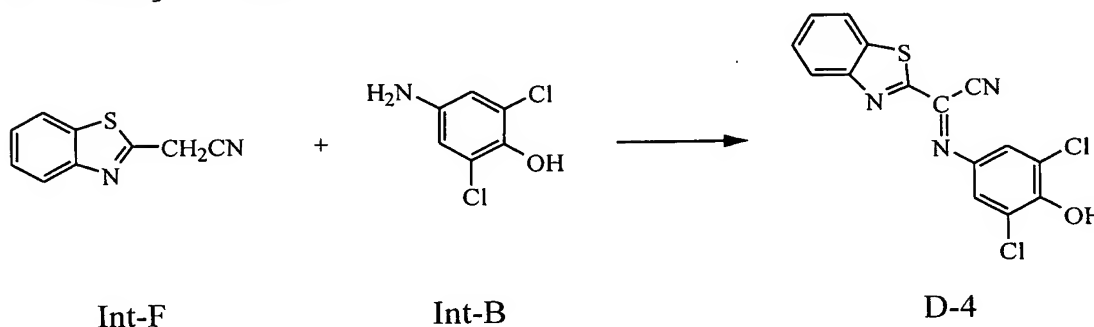


To 50 mL of ethyl acetate were added 2.59 g of N-(1-phenyl-5-pyrazolon-3-yl)pivaloylamide (Int-E) and 2.8 mL of triethylamine. The resulting mixture was stirred at room temperature. After addition of 2.20 g of commercially available 2,6-dichloroquinone-4-chloroimide (Int-D) in several portions, stirring was continued for 2 hours. The reaction mixture was washed with dilute hydrochloric acid. The organic layer was washed with water twice, dried over

anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column (eluent: 2:1 mixed solvent of chloroform and ethyl acetate). The eluate was concentrated under reduced pressure. Acetonitrile (10 mL) was added to the residue to crystallize the same. The crystals thus precipitated were collected by filtration, washed while pouring a small amount of acetonitrile thereon, and air dried, whereby 0.44 g of Exemplified Compound D-51 was obtained as crystals (yield: 10%).

Synthesis 4 <Synthesis of Exemplified Compound D-4>

Synthesis was conducted in accordance with the following scheme.



Benzothiazol-2-yl-acetonitrile (Int-F, 3.48 g), 3.92 g of commercially available 4-amino-2,6-dichlorophenol (Int-B), 16.6 g of anhydrous potassium carbonate, 60 mL of ethyl acetate, 40 mL of water and 20 mL of ethanol were mixed. The resulting mixture was stirred at room temperature. To the reaction mixture was added 11.0 g of ammonium persulfate in 6 portions over 30 minutes and

stirring was continued for 2 hours. The reaction mixture was filtered under reduced pressure. The cake on the Nutsche was added to 120 mL of water and the mixture was stirred at room temperature. Concentrated hydrochloric acid was added slowly to make the reaction mixture acidic (about pH 3 when measured by pH test paper). The crystals were collected by filtration and washed while pouring thereon 60 mL of water and then air dried, whereby 5.24 g of Exemplified Compound D-4 was obtained as yellowish brown crystals (yield: 75%).

Examples 1 to 4

Hair dye foams as shown in Table 1 were prepared in a manner known per se in the art.

Table 1

Component (wt.%)	Examples			
	1	2	3	4
Dye (D-50)	0.5	-	-	-
Dye (D-38)	-	0.5	-	-
Dye (D-51)	-	-	0.5	-
Dye (D-4)	-	-	-	0.5
Monoethanolamine	1	1	1	1
Ethanol	15	15	15	15
Propylene glycol	10	10	10	10
Polyoxyethylene (20) octyldodecyl ether	10	10	10	10
Polyoxyethylene (9) tridecyl ether	3	3	3	3
Polyoxyethylene (3) tridecyl ether	6	6	6	6
Oleic diethanolamide	8	8	8	8
Oleyl alcohol	2	2	2	2
Ammonium chloride	q.s. *1	q.s. *1	q.s. *1	q.s. *1
LPG (4.0 kg/cm ²)	10	11	12	12
Purified water	Balance	Balance	Balance	Balance

*1: an amount to adjust the pH to 8.5

The above-described hair dye foams were each applied

to the goat hair at 30°C and was caused to act on the hair for 20 minutes. The hair thus dyed was then washed with an ordinarily used shampoo, followed by drying. As a result of the observation of the color tone of the dyed hair, it exhibited good dyeing property and resistance to shampoo.

Examples 5 to 9

Two-part hair dyes as shown in Table 2 were prepared in a manner known per se in the art.

Table 2

Component (wt.%)		Examples				
		5	6	7	8	9
1-st part	Dye (D-50)	0.5	-	-	0.5	-
	Dye (D-38)	-	-	0.5	-	-
	Dye (D-51)	-	-	-	-	0.5
	Dye (D-4)	-	0.5	-	-	-
	HC Red 3	-	-	0.2	-	-
	p-Aminophenol	-	-	-	0.2	0.2
	p-Amino-o-cresol	-	-	-	0.2	0.2
	Ammonia (28 wt.%)	6	6	6	6	6
	Ethanol	15	15	-	-	-
	Propylene glycol	10	10	2	2	2
	Polyoxyethylene (20) octyldodecyl ether	10	10	-	-	-
	Polyoxyethylene (40) cetyl ether	-	-	2	2	2
	Polyoxyethylene (2) cetyl ether	-	-	2.5	2.5	2.5
	Oleic diethanolamide	8	8	-	-	-
	Oleyl alcohol	2	2	-	-	-
	Stearyltrimethylammonium chloride	-	-	1.5	1.5	1.5
	Cetanol	-	-	1	1	1
	Liquid paraffin	-	-	0.5	0.5	0.5
	Ammonium chloride	q.s *2	q.s *2	q.s *2	q.s *2	q.s *2
	Sodium sulfite	-	-	-	0.5	0.5
	Tetrasodium edetate	0.1	0.1	0.1	0.1	0.1
	Purified water	Balance	Balance	Balance	Balance	Balance
2-nd part	Hydrogen peroxide	6	6	6	6	6
	Methyl paraben	0.1	0.1	0.1	0.1	0.1
	Phosphoric acid	q.s. *3	q.s. *3	q.s. *3	q.s. *3	q.s. *3
	Purified water	Balance	Balance	Balance	Balance	Balance

*2: an amount to adjust the pH to 9.8.

*3: an amount to adjust the pH to 3.5

After 1 part by weight of the first part was mixed with 1 part by weight of the second part, the resulting mixture was applied to the goat hair at 30°C and was caused to act on the hair for 20 minutes. The hair thus dyed was then washed with an ordinarily used shampoo, followed by drying. As a result of the observation of the color tone of the dyed hair, it exhibited good dyeing property and resistance to shampoo.